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PHYSICOCHEMICAL PROPERTIES OF MAGNETICALLY SEPARATED SHALE OIL SOLIDS

By

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INTRODUCTION

The application of high gradient magnetic separation (HGMS) to shale oil has been shown by the authors (1) to be an effective method for the removal of solid particles from these hydrocarbon streams. Typical ash removal results indicated that the solids concentration was reduced by 90-100% in several different types of shale oils and that temperature effects can be significant. Similar studies (2-5) of coal and other synthetic fuels have demonstrated the usefulness of this technique in removing inorganic particulates, such as iron sulfides and pyrite, from liquid hydrocarbon streams. The application of magnetic separation methods to coal-derived liquids has been prompted by the large concentrations of iron-containing compounds present in coal ash. By comparison, the mineral matter composition of most oil shales is not as rich in iron. However, the iron composition appears to be fairly evenly distributed enabling even very small solid particles to be efficiently separated from shale oil streams.

The separation of solids from shale oil is believed to substantially simplify shale oil processing and upgrading technologies through the reduction of concomitant plugging, stability and pollution problems. An earlier paper by the authors (1) discussed the major features of the magnetic separation procedure and presented preliminary solids characterization data. The purpose of this study was to further define the nature of the separated solids and apply these results not only to the development of improved shale oil processing methods, but also to a better fundamental understanding of other organic/mineral matter systems.

In contrast to other magnetic separation techniques, HGMS is capable of separating weakly paramagnetic particles in addition to the ferromagnetic components from a bulk fluid, such as the hydrocarbon streams derived from oil shale. Magnetic separation is a physical separation process based on the interaction of four types of competing forces: tractive magnetic, gravitational, hydrodynamic and interparticle. Therefore, the quantity and quality of the separation depend both on the nature of the feed and the variable HGMS operating parameters, such as velocity, temperature, magnetic field strength, etc. Important properties of the feed to be considered include particle radius, kinematic viscosity, fluid density and the magnetic susceptibility of the particle and fluid. These latter parameters are particularly relevant to this solids characterization study. (The effects of HGMS process variables were discussed in (1)).

The typical HGMS apparatus consists of a canister filled with a ferromagnetic matrix and surrounded by a solenoid magnet. This type of separator is frequently referred to as an induced pole device, because the magnet acts upon the matrix to produce strong inhomogeneous magnetic fields which in turn generate high field gradients at the edges of the matrix filaments. These high field gradients then attract magnetic particles to the filaments, thereby trapping and separating them. Both the solids-free fluid and the trapped particles are recoverable.

The shale oil solids were characterized using several analytical techniques, including X-ray diffraction, X-ray fluorescence and thermomagnetic measurements. Similar studies of coal liquefaction mineral particulates (5) and coal filter cake solids (6) have been published. At the completion of this work, a brief report (7) describing the removal of mineral particles from shale oil by magnetic separation became available. Their proposed method (7) consists of heating the oil shale feed to at least the magnetic transformation temperature of the majority of the solids and then applying a magnetic field to the retorted shale oil in order to separate the solids from the hydrocarbon stream. Their magnetization measurements were of Green River oil shale (7), whereas this study is the first to report on the physicochemical properties of the magnetically separated shale oil solids. Certain fundamental characteristics of the separation of solids from shale oil have been obtained from single wire HGMS experiments investigating the buildup process itself (8).

Takayasu et al. (8) also presented preliminary magnetization data of the solids separated in those experiments.

EXPERIMENTAL

The HGMS apparatus and the shale oil feed samples have been described previously (1) and only a brief summary will be given here. Samples of shale oil effluent were treated using a pilot-scale commercial HGMS system. The canister volume was filled with a stainless steel wool matrix (Type 430) to which magnetic fields as large as 2T (20 kOe) were applied. The HGMS unit was equipped with various flow, temperature and pressure controllers such that fluctuations in the experimental conditions were small. Typical process variable conditions were as follows: flow rate, 10-700 ml/min; temperature, 50-250°C; pressure, 0.17 MPa. Trapped solid particles were removed from the matrix material at the completion of the separation cycle using a fixed toluene back-flush flow with the magnetic field turned off.

Three different types of shale oils were studied representing a range of mineral matter composition, organic carbon content and retorting conditions: Paraho, Addington and Moroccan. These oils were obtained from Western U. S., Eastern U. S. and Moroccan oil shales, respectively (1). The initial ash contents of these shale oils were found to vary from 130 to 9500 ppm. As mentioned earlier, the ash removal efficiencies were generally very good, as high as 100% for the Addington sample (see Table I, Reference 1).

TABLE I
BULK MINERALOGY OF SHALE OIL SOLIDS

Shale Oil	Clay	SiO ₂	FeO(OH) (wt %)	Feldspar	Amorphous ^a
Paraho	6	3	trace	trace	90
Moroccan	4	2	14	trace	80
Addington ^b	40	16	--	2	42

a. Mostly iron sulfide.

b. Pyrrhotite (Fe_{1-x}S) was identified in this sample.

The bulk mineralogy and elemental composition of the solids were determined using X-ray diffraction and X-ray fluorescence, respectively. Magnetic measurements were based on the Faraday technique using Sucksmith type pole pieces (9). Low temperature data were obtained using a 12-inch electromagnet from Pacific Electric Motor Company (type 12A-HI-A). The high temperature magnetic measurements involved a Varian Model V-400T electromagnet and a Cahn electrobalance.

CHARACTERIZATION OF SHALE OIL SOLIDS

X-Ray and Elemental Analysis

The Western (Green River Formation) oil shale, Paraho, contains relatively large concentrations of carbonate and silicate minerals in its natural state prior to retorting. The Moroccan oil shale has a similar bulk mineralogy, but in contrast to these oil shales, the Addington sample is predominantly composed of silicate minerals. These mineral compositions can be compared with the bulk mineralogy of the various separated solids summarized in Table I. The major minerals identified in the solids were clay, quartz, FeO(OH) and iron sulfide. Not surprisingly, the silicate-based Addington oil shale generated shale oil solids containing relatively large concentrations of clay and SiO₂. Since these minerals are not inherently magnetic, the data suggest a uniform distribution of iron sulfide and ferrimagnetic pyrrhotite (mass magnetic susceptibility ~0.125 emu/g) among the mineral solids and a close chemical/physical association between silicate minerals and iron-containing compounds, such as iron sulfide and pyrrhotite.

Relatively larger concentrations of amorphous material, mostly iron sulfides, were identified in the Paraho and Moroccan solids than the Addington solids. These results are consistent with the elemental composition data which indicate a substantially smaller Fe content for the Addington solids (see Table II). Although 100% ash removal was obtained from the Addington shale oil, the separated solids are relatively deficient in iron-containing compounds. Thus, factors in addition to magnetic susceptibility (e.g., average particle diameter) need to be considered in the separation of shale oil solids using HGMS (1). The major elemental constituent of the Addington solids was Si, further suggesting the possibility of an iron-silicon association. In addition, these

solids had a relatively larger concentration of elemental Al, K and Ti. The magnetic susceptibilities of such compounds are not insignificant, although substantially less than that of most Fe-containing compounds.

The organic C, H, O, N and S concentrations in the original shale oil feed compared to the separated solids were determined by conventional elemental analysis. These results (see Table III) indicate that the relative heteroatom concentration in the organic matter separated along with the solid particles is significantly enhanced. The reported increases in the O/C, N/C and S/C ratios are not due solely to a mechanical filtration procedure, but rather demonstrate the added usefulness of the HGMS method (Mechanical filtration involved passing a 1:200 shale oil : hexane mixture through a 0.125 micron filter). Thus, in addition to removing solid particles from shale oil streams, the overall quality of the resulting oil may also be improved.

TABLE II
ELEMENTAL COMPOSITION OF SHALE OIL SOLIDS

Element (Wt %)	Paraho	Moroccan	Addington
Ash	41.4	50.6	60.1
Al	0.7	0.6	1.3
Ca	4.6	0.6	0.6
Cr	<0.1	1.1	<0.1
Fe	11.4	22.2	4.5
K	1.5	0.6	3.3
Mn	0.2	0.2	0.1
P	0.8	0.6	0.4
S	10.2	7.8	3.1
Si	4.5	1.8	7.5
Ti	0.7	0.5	0.8
Others	As, Cu, avg, Ni, Zn	As, Cu, avg, Zn	As, Cu, avg, Ni, Zn

TABLE III
ELEMENTAL ANALYSIS OF ORIGINAL SHALE OIL AND
MAGNETICALLY SEPARATED SHALE OIL SOLIDS

Element/ Atomic Ratio	Paraho		Moroccan		Addington	
	Original	Solids	Original	Solids	Original	Solids
Ash (wt %)	0.039	41.4 (----)	0.013	50.6	0.95	60.1
C (wt %)	83.4	29.4 (61.8)	79.5	25.7	-	30.1
H (wt %)	11.1	3.3 (6.6)	9.6	2.3	-	2.1
O (wt %)	2.2	17.4 (----)	2.2	12.3	-	5.0
N (wt %)	2.1	3.7 (3.6)	1.3	2.6	-	1.4
S (wt %)	0.88	5.7 (5.1)	7.7	6.6	-	2.3
H/C	1.59	1.33 (1.27)	1.44	1.07	-	0.83
O/C (x100)	2.0	4.4 (-----)	2.1	36	-	12
N/C (x100)	2.2	11 (5.0)	1.4	8.7	-	4.0
S/C (x100)	0.4	7.3 (3.1)	3.6	9.6	-	2.9

() Solids obtained using 0.125 micron filter.

Thermomagnetic Studies

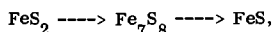
The thermomagnetic behavior of the shale oil solids was studied in the temperature range 4.2 to 1000K and in applied fields, H, up to 20 kOe. The accuracy of the experimental results are estimated to be approximately $\pm 6\%$. A typical experimental data plot of pulling force versus temperature is shown in Figure 1 for the Paraho solids at H=0 and 5 kOe. The pulling force at H=5 kOe was found to decrease with increasing temperature reflecting mainly thermal decomposition processes of organic matter and carbonate minerals which are essentially complete by about 900°C as is evidenced by the H=0 kOe data (i.e., standard thermogravimetric analysis (TGA)). Typical weight loss values due to thermal decomposition were about 40-60% (see Tables II and III).

The dependence of magnetization, σ (emu/g), on temperature and external magnetic field

are shown in Figures 2-4. The $\sigma(T)$ plots, Figures 2 and 3, were calculated based on the differences in pulling force with the magnetic field on and off (see Figure 1) at each temperature and the standard calibration between pulling force and magnetization. The magnetizations per gram at room temperature and 5 kOe for each sample were determined to be the following: Paraho - 0.85, Moroccan - 0.77 and Addington - 0.42.

The magnetizations of the Paraho and Moroccan solids, as a function of temperature over the range 25 to 900°C, were qualitatively similar (see Figure 2). Three distinct peaks were observed at an applied field of 5 kOe, although the magnetization was significantly larger for the Moroccan solids at temperatures above ~250°C, a magnetic transformation temperature (the Moroccan solids also contained the highest relative Fe concentration). This higher magnetization may be attributed to an intrinsically larger concentration of materials with higher magnetic susceptibilities at elevated temperatures. For example, it is believed that certain components, such as pyrites, interact with water present in other minerals at the magnetic transformation temperature or higher temperatures to form materials having a higher magnetization (7).

The data suggest that as the temperature is increased, the solids undergo various decomposition, chemically reactive and/or inductive processes resulting in the formation of magnetically active material. The highest temperature peak, 700-800°C, is attributed to the formation of Fe^0 and the onset of the phase transition at the Curie point from paramagnetic to ferromagnetic character. The origin of the iron may involve the reduction of Fe^{+3} or Fe^{+2} species by carbon-containing compounds present in the shale oil stream. The two peaks at lower temperatures, ~300 and 500°C, do not appear to be directly attributable to specific iron carbide or iron oxide compounds, although mineral matter effects or carbon-hydrogen bonding could possibly account for the shift of standard Curie points. The lower temperature peak may correspond to the reaction sequence



since pyrrhotite, Fe_7S_8 , is strongly ferrimagnetic (Curie point ~300°C) and FeS_2 and FeS have zero and very low magnetizations, respectively (10). Pyrrhotite was identified in the Addington samples. The sharp increase in magnetization between ~400-500°C for the Paraho and Moroccan solids may be due to the transformation of iron sulfides, FeS or FeS_2 , to Fe_3O_4 or gamma - Fe_2O_3 and the subsequent decline to the formation of alpha- Fe_2O_3 or FeO .

As Figure 2 indicates, the Addington thermomagnetograph differs distinctly from that of the Paraho and Moroccan solids. In general, the magnetization was observed to be essentially constant with temperature. The absence of pronounced maxima at ~500 and 750°C, as in the case of the Paraho and Moroccan samples, probably reflects the relatively low concentrations of iron sulfides and Fe-containing compounds in the Addington oil shale solids. However, the Addington solids did exhibit a Curie point for α -Fe upon cooling. The magnetization at room temperature for these solids was found to increase to 0.86 emu/g after the temperature treatment. If the magnetic pull is due entirely to Fe, then 7.0×10^{-6} g of ferromagnetic iron in 25.6 mg of sample, or 0.03 wt % Fe, was produced during the heating process assuming no weight loss.

Low temperature data, 4 to 273K, were obtained at two different field strengths, 4 and 20 kOe (see Figure 3). Analogous to the higher temperature results, the Paraho and Moroccan solids exhibit similar thermomagnetic behavior, however, the magnetization is significantly larger between 4 and 30K for the Paraho solids at both field strengths. The 4 and 20 kOe data for these two samples are distinctly displaced from one another, with larger magnetizations associated with the 20 kOe curves, but in contrast, essentially identical $\sigma(T)$ dependences were obtained for the Addington solids, with the exception of the small temperature range from 4 to 30K. In general, the Addington solids have a lower magnetization in the low temperature regime, although the magnetization increases and approaches that of the Moroccan solids with $H=4$ kOe between 4 and 60K. The upper temperature portion of the curves in Figure 3 confirm the earlier room temperature magnetization results reported above (see Figure 2) indicating the data to be self-consistent.

The similarity of the Addington and Moroccan magnetizations between 4 and 60K was observed to remain essentially unchanged as a function of external field. Plots of magnetization versus external field at 4.2K are shown in Figure 4. Whereas the Addington and Moroccan curves are almost superimposable, the Paraho solids exhibit much larger magnetizations over the entire range of external field studied. However, the relative increase in magnetization with temperature is comparable for all three samples.

On the basis of the magnetometric data, it appears that all the solid samples are a mixture of a weak ferromagnetic phase, indicated by the low field portion of the $\sigma(H)$ curves in Figure 4, and a paramagnetic phase. The paramagnetic phase seems to reflect the behavior characteristic of Curie-Weiss type materials and appears to be more pronounced than the ferromagnetic phase. The Paraho and Moroccan samples showed significantly larger magnetizations than the Addington solids. This weak magnetization was particularly evident by the almost flat dependence of the magnetization on temperature. In addition, the magnetization versus external field curve for the Addington solids

Figure 1

**THERMOMAGNETIC and THERMOGRAVIMETRIC BEHAVIOR of
PARAHO SHALE OIL SOLIDS from 25 °C to 920 °C (CYCLES in Ar)**

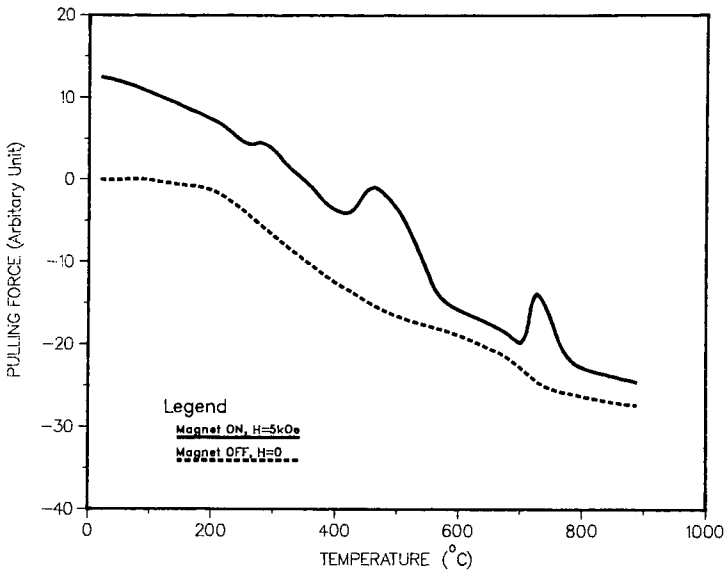


Figure 2

**PLOTS of MAGNETIZATION vs TEMPERATURE
for SHALE OIL SOLIDS**

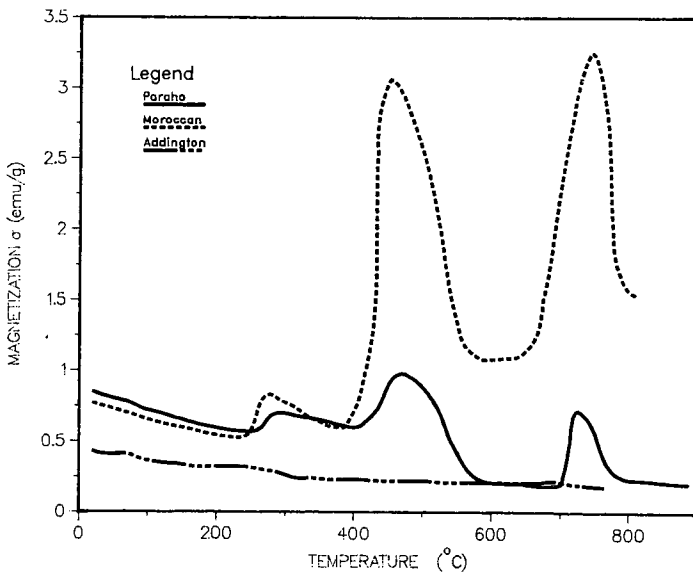


Figure 3

**MAGNETIZATION - TEMPERATURE CURVES for SHALE OIL SOLIDS
at LOW and HIGH EXTERNAL FIELDS (4 & 20 kOe)**

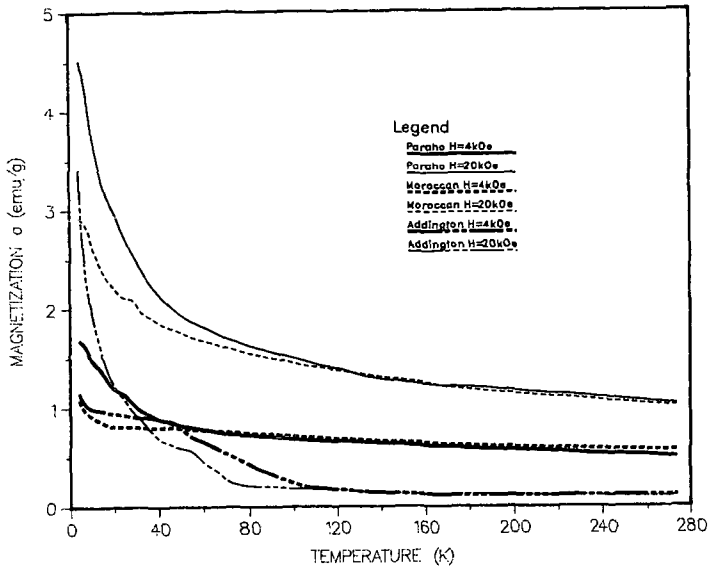
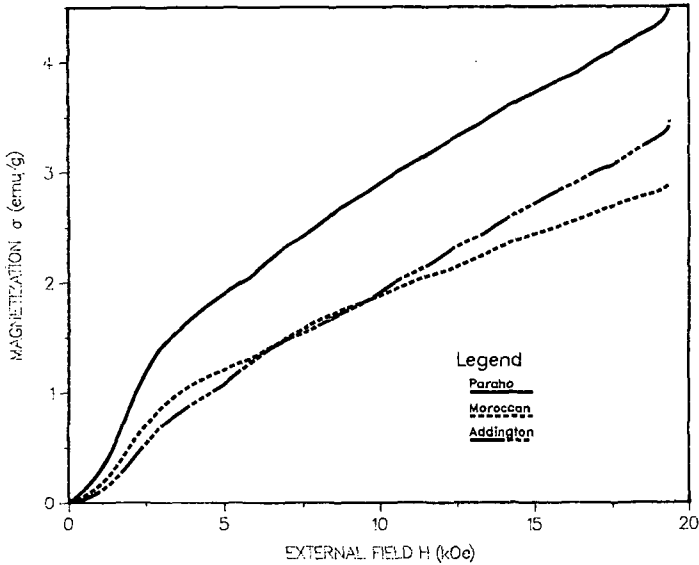


Figure 4

**MAGNETIZATION - FIELD STRENGTH CURVES
for SHALE OIL SOLIDS**



was nearly linear, in contrast to some degree of curvature for the Paraho and Moroccan solids. This suggests that the Addington solids are mainly paramagnetic, consistent with the bulk mineralogy and elemental composition results discussed above. It should be noted that magnetometric measurements reflect the average bulk magnetic moment of the sample as a whole. Therefore, when considering mixtures of different magnetic phases, the results are representative of averaged quantities over all phases.

SUMMARY AND CONCLUSIONS

Thermomagnetic and X-ray studies have shown that the composition of shale oil solids magnetically separated from three different shale oil feeds are distinctly varied, but that high ash removal efficiencies are, nonetheless, obtainable under appropriate conditions for all three shale oils investigated. A clear example is the Addington sample which yielded 100% ash removal due to high average particle diameters, despite the lowest magnetization as a function of temperature among the three shale oil solids. On the basis of the magnetic behavior exhibited by the shale oil solids, a qualitative measure of the different phase transformations and the species present was obtained. These data reflected the general occurrence of a paramagnetic phase mixed with a trace amount of a ferromagnetic component. This conclusion is consistent with the bulk mineralogy and elemental composition results for the shale oil solids. These results may have potential application to the design of a larger scale magnetic separation system and the choice of operating parameters.

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